Solvent Effect on Junction Size in Syndiotactic Polystyrene Physical Gel

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ABSTRACT: In order to estimate the junction point size ζ of syndiotactic polystyrene (sPS) physical gels formed in chloroform, toluene, benzene, and *o*-dichlorobenzene, gel-melting temperatures were measured as a function of polymer concentration. The size ζ in number of styrene units was estimated with the aid of the Tanaka and Stockmayer theory (TS theory), which is based upon the conjecture that junction points of a gel are aggregates comprised of ζ units in length and ρ sequences in cross section. According to measurement of *in situ* FT-IR, the junction points of sPS/organic solvent gels were suggested to be aggregates of sPS chains with helical structure of TTGG conformation regardless of the difference in solvents. Quantitative analysis by the TS theory led to the results that the size ζ was little dependent upon the sPS molecular weight for each sPS/organic solvent system. On the other hand, the size ζ was strongly affected by solvents, *i.e.*, ζ in sPS/*o*-dichlorobenzene gel was the largest among the solvents used in the present study, while that in sPS/chloroform gel was the smallest. This solvent effect on the junction point size ζ probably arises from the difference in magnitude of polymer/solvent interaction. [DOI 10.1295/polymj.37.294]

KEY WORDS Syndiotactic Polystyrene / Polystyrene / Thermoreversible Gel / Junction Size / Gel-melting Temperature / Time-resolved FT-IR /

Syndiotactic polystyrene (sPS) is of considerable scientific and industrial interest as a rigid high performance semicrystalline material. It is known that sPS polymer has two types of molecular chain conformations in its crystalline region: one is the all-*trans* planar zigzag structure (TT), and the other is the helical conformation (TTGG).^{1–5}

Like other crystalline or semicrystalline polymers, sPS polymer also converts to thermoreversible gel in suitable organic solvents such as toluene or chloroform. Kobayashi *et al.* investigated the gelation process of sPS with time-resolved Fourier transform infrared (FT-IR) spectroscopy and showed that highly ordered TTGG conformations are formed on gelation.⁶ Recent studies in the temperature–concentration phase diagrams of sPS gels have suggested that solvent molecules are intercalated between sPS chains in the TTGG conformation, and the number of solvent molecules involved is dependent on the gelation solvent.^{7–11} The ordered TT conformation was observed on gelation of sPS in big size solvent like octadecyl benzoate.¹² Time-resolved small-angle neutron scattering (SANS) experiments also showed that the gel-network structure formation occurred in parallel to the conformational ordering of sPS chains.¹³

The thermoreversible gelation of highly stereore-

gular polymers such as sPS and syndiotactic poly(methyl methacrylate) is considered to proceed in two steps:^{14–16} A first step is an intramolecular coil-to-helix transition; This change in molecular conformation is then followed by an intermolecular association of multiple helix segments, which leads to the formation of network structure. This gelation mechanism is very similar to that of biopolymers like carrageenan and agarose.^{17–19}

Although there have been much research so far on sPS/organic solvent gels, the structure and the size of crystalline junctions is still a matter of debate. The present study aims to estimate the crystalline junction size ζ of sPS gels by using the Tanaka and Stockmayer theory,^{20,21} which is based upon the conjecture that junction points of a gel are aggregates comprised of ζ units in length and ρ sequences in cross section. The effects of solvent and sPS molecular weight on the junction size ζ were then investigated by using four kinds of solvents and five sPS samples with different molecular weights.

EXPERIMENTAL

Materials

All sPS samples were kindly supplied by Idemitsu

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Petrochemical Co., Ltd., and used as received. The content of syndiotactic pentads measured by ^{13}C NMR is over 99%. The weight-average molecular weights ($\bar{M}_w$) of each sPS are 31.7×10^4 (sample code: sPS-32), 23.3×10^4 (sPS-23), 19.1×10^4 (sPS-19), 15.2×10^4 (sPS-15), and 12.9×10^4 (sPS-13). As gelation solvents, chloroform, toluene, benzene, and *o*-dichlorobenzene (special-grade reagent from Kanto Chemical Co., Inc.) were used without further purification.

Fourier Transform Infrared (FT-IR) Measurement

Time-resolved FT-IR measurements were performed with a JASCO FT-IR spectrometer, Model FT/IR-660. The sPS powder was first completely dissolved into the gelation solvent at the concentration of 3 wt % and then the solution was rapidly poured into a KRS-5 cell placed in the FT-IR spectrometer. The FT-IR spectra were recorded by the ATR (attenuated total reflection) method at intervals of 10 s with the wavelength resolution of 4 cm^{-1} .

Gel-melting Temperatures

It is well known that gel-melting temperature (T_m^g) of crystalline polymer does not coincide with the temperature at which the last trace of crystallites has melted away.²² In a sol, large numbers of crystallites still exist. Therefore, measurement of gel-melting temperature by using DSC is not adequate. In the present study, gel-melting temperatures were measured by the falling-ball method.²³ A given amount of sPS and a gelation solvent were placed in a sealed glass tube with 8 mm-diameters. The glass tube was kept in an oil bath at $120\text{--}180^\circ\text{C}$ until homogeneous solution was formed and then the solution was quickly quenched by putting the glass tube into a water bath at 30°C to prepare a gel. A steel ball of *ca.* 30 mg weight was placed at the surface of the gel layer. The gel was heated at the rate of *ca.* $0.3^\circ\text{C min}^{-1}$ and the height of the steel ball from a reference level was measured by a cathetometer at selected temperatures. When the gel melted, the steel ball began to fall. The gel-melting temperature was determined by the method of Takahashi.²³ In our previous study,²⁴ the dependence of T_m^g on the weight of the steel ball was estimated prior to a series of experiments, and the steel ball of *ca.* 30 mg weight with 2 mm diameter was chosen on this basis.

RESULTS AND DISCUSSION

Conformation of sPS Chains in Gel

We first investigated the conformational ordering process on gelation of sPS/organic solvent systems. Infrared spectroscopy is a very sensitive tool to exam-

ine the conformation of polymer chains and thus the conformation of sPS chains in the gel was measured with *in situ* FT-IR spectroscopy. Figure 1 shows the time-resolved IR spectra of (a) sPS-19/chloroform gel, (b) sPS-19/benzene gel, (c) sPS-19/toluene gel, and (d) sPS-19/*o*-dichlorobenzene gel in the wave-number range $500\text{--}600\text{ cm}^{-1}$. This range is known to be sensitive to sPS conformation.^{1,25} It can be seen from Figure 1 that the same strong vibrational bands near 572 , 549 , and 536 cm^{-1} for all solvents were observed and these bands became larger with increasing time. These bands are characteristic of the conformation TTGG, indicating that the sPS chains gather together into the helical structure in the sPS/organic solvent gel. It can be concluded from these results that the junction points in the gel consist of aggregates of sPS chains of the helical structure with ζ styrene units in length and ρ sequences as shown in Figure 2.

Figure 1 also shows that the type of the ordered conformation was independent on the solvents used in this study, but the rate of gelation was strongly dependent on the solvent. The gelation of sPS/chloroform systems took place very slowly compared with other solvents, suggesting that chloroform would behave as relatively good solvent for sPS over other solvents. The junction point size ζ of the gel may therefore differ among the solvents. We have tried to estimate the size ζ from the TS theory.

Junction Point Size of Gel

In order to estimate the junction size ζ in sPS gels from the TS theory, gel-melting temperatures (T_m^g) were measured as a function of polymer concentration. Figure 3 shows T_m^g of sPS-19 gels plotted against the polymer concentration (C). We used toluene, *o*-dichlorobenzene, benzene, and chloroform as gelation solvents. Gel-melting temperature in each solvent increased gradually with an increase in the polymer concentration and also strongly depended upon the gelation solvents.

Tanaka and Stockmayer derived the following equation for gel-melting temperatures of polymer, assuming the junction points of gel to be aggregates comprised of ζ units in length and ρ sequences in cross section:

$$\ln C = \zeta \frac{\Delta h_0}{k_B \cdot T_m^g} - \frac{1}{\rho - 1} \ln M + \text{const.} \quad (1)$$

where C is the polymer concentration, k_B is the Boltzmann constant, Δh_0 is the enthalpy of bonding, ρ is the junction multiplicity (*i.e.*, the number of chains which enter into a single junction point), and M is the molecular weight of polymer.

Equation 1 suggests that a plot of $\ln C$ vs. $10^3/T_m^g + \ln M$ at constant M gives a straight line for each

Figure 1. Time-resolved infrared spectroscopy of (a) sPS-19/chloroform gel, (b) sPS-19/benzene gel, (c) sPS-19/toluene gel, and (d) sPS-19/*o*-dichlorobenzene gel.

Figure 2. An illustration of the crystalline junction point with helical structure in sPS gels.

solvent. The plots for sPS-19/organic solvents gels are shown in Figure 4. As the present samples are polydisperse, weight-average molecular weight ($\bar{M}_w$) is used for M in eq 1. A linear relationship was found to hold between $\ln C$ and $10^3/T_m^g + \ln \bar{M}_w$ and thus eq 1 is considered to be applicable to sPS thermoreversible gels. In the TS theory, the slope of the straight line is equal to the term $-\zeta|\Delta h_0|/(10^3 k_B)$ ($\equiv A$). The junction point size ζ is, therefore, obtained by the following equation:

$$\zeta = -\frac{10^3 k_B}{|\Delta h_0|} \times A = -\frac{10^3 R}{|(\Delta h_0)_{\text{mol}}|} \times A \quad (2)$$

where $(\Delta h_0)_{\text{mol}}$ is the enthalpy of bonding per mole

Figure 3. Gel-melting temperatures (T_m^g) as a function of polymer concentration (C).

of the repeating units and R is the gas constant. The size ζ was calculated by using the numerical values of $(\Delta h_0)_{\text{mol}} = 2.0 \text{ kcal mol}^{-1}$ ²⁶ and $10^3 R = 1.9864 \text{ kcal mol}^{-1} \text{ K}^{-1}$. The junction size ζ as a function of the molecular weight $\bar{M}_w$ is shown in Figure 5.

As seen in Figure 5, the junction size ζ was little dependent upon the molecular weight $\bar{M}_w$ for each

Figure 4. Relation between $\ln C$ and $10^3/T_m^g + \ln \bar{M}_w$.

Figure 5. Effects of the gelation solvent and the sPS molecular weight $\bar{M}_w$ on the junction size ζ .

sPS/organic solvent system. On the other hand, the gelation solvent strongly affected the junction size in sPS gels. The size ζ in sPS/organic solvents gels increased in the order chloroform/sPS gel < benzene/sPS gel < toluene/sPS gel < *o*-dichlorobenzene/sPS gel. It can be seen from Figure 3 that T_m^g of the sPS gels became higher with this order. We have reported that the junction size ζ of linear low-density polyethylene gels increased with increasing polymer–solvent interaction parameter (χ_{12}).^{27,28} We have also shown that T_m^g of poly(vinylidene fluoride) or poly(butylene succinate) gels increases with increasing χ_{12} .^{29,30} In view of these previous results, the junction size ζ in sPS gels is thought to have a close relationship to the sPS–solvent interaction parameter though we have not measured χ_{12} yet. That is to say, the size ζ is presumed to become larger with increasing χ_{12} . The results will be reported elsewhere.

CONCLUSIONS

The present study clarifies the following results for the gelation of sPS in organic solvents:

1. The crystalline junction size ζ in number of styrene units becomes smaller in a relatively good solvent.
2. The thermoreversible gelation occurs as sPS chains are taking the TTGG conformation.

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